Electronic supplementary information (ESI)

Nitrogen doped carbon dots as fluorescence ON-OFF-ON sensor for parallel detection of copper (II) and mercury (II) ions in solutions as well as in filter paper based microfluidic device

Khemnath Patir and Sonit Kumar Gogoi*

Department of Chemistry, University of Gauhati, G. B. Nagar, Guwahati -781014, Assam, India. E-mail:guchem.gogoi@gmail.com, Patirkhemnath@gmail.com





Figure S1.(a) Particle size disributuionof NCDs from TEM images(b) Particle size distribution profile from dynamic light scattering (DLS) measurement of NCDs (c) Zeta Potential measurement of NCDs (d) FT-IR spectra of NCDs (different mol ratio, 3:1, 6:1,9:1, 12:1 of urea and EDTA.)(e) FT-IR spectra of NCDs (different temperature, 200, 250, 300°C)



Figure S2.(a) UV- visible spectra of NCDs (different molar ratio, 3:1, 6:1,9:1, 12:1 of urea and EDTA.) (b) UV-visible spectra of NCDs (different temperaure, 200, 250, 300°C) (c) Normalized fluorescence spectra of NCDs (different molar ratio, 3:1, 6:1,9:1, 12:1 of urea and EDTA, $\lambda_{ex} = 320$ nm) (d) Normalized fluorescence spectra of NCDs(different temperaure, 200, 250, 300°C, $\lambda_{ex} = 320$ nm)



Figure S3.(a) Qautum yield determination of NCDs (b) variation of the qauntum yield of NCDs (different molar ratio,3:1, 6:1,9:1, 12:1 Urea:EDTA) (c) TRPL life time profile of NCDs.(inset: fluorescence life time table)



Figure S4. (a) Fluorescence emission responses of aqueous NCDson addition of Cu²⁺(25 μ M) ions with variation of time($\lambda_{ex} = 360$ nm) (b) Plot of F / F_ovs time, error bars are derived from three independent sets of experiments. (c) Fluorescence emission responses of aqueous NCDs on addition of Hg²⁺ (25 μ M) ions with variation of time ($\lambda_{ex} = 360$ nm) (d) Plot of F / F_ovs Hg²⁺time, error bars are derived from three independent sets of experiments.



Figure S5. (a) Fluorescence emission spectra of NCDs before and after addition of mixture of Cu²⁺⁺ Hg²⁺ ([Mⁿ⁺] =50 μ M, 5 μ L + 5 μ L)and follow by addition of different concentration of trisodium citrate (SC)(λ_{ex} = 360 nm) (b) corresponding relative fluorecence ratio of the NCDs with variation of the concentration of SC (c) Fluorescence emission spectra of NCDs before and after addition of mixture of Hg²⁺ + Cu²⁺ ([Mⁿ⁺] =50 μ M, 5 μ L + 5 μ L) and follow by addition of different concentration of vitamin C (Vit C) (λ_{ex} = 360 nm) (d) corresponding relative fluorecence ratio of the NCDs with variation of the concentration of Vit C.



Figure S6. (a) Fluorescence emission responses of aqueous NCDs on addition of $Cu^{2+}(0-25 \ \mu M)$ ions (in tap water)with excitation fixed at 360 nm wavelength (b) Plot of F_0/F vs Cu^{2+} concentration (0-25 μ M), error bars are derived from three independent sets of experiments.(c) Fluorescence emission responses of aqueous NCDs on addition of Hg²⁺ (0-25 μ M) ions (in tap water)withexcitation fixed at 360 nm wavelength(d) Plot of F_0/F vs Hg²⁺ concentration (0-25 μ M), error bars are derived from three independent sets of experiments.



Figure S7.(a) Fluorescence intensity of the NCDs towards ionic strenght (NaCl) (0.1 to 1mM)($\lambda_{ex} = 360$ nm)(b) corresponding fluorescence intensityversus ionic concentration plot (c) Fluorescence intensity of the NCDs with time($\lambda_{ex} = 360$ nm)(d) corresponding fluorescence intensity plot.



Figure S8. (a) Fluorescence spectra of NCDs at $pH(2-12)(\lambda_{ex} = 360 \text{ nm})$ (b) corresponding bar diagram



Figure S9.Digital photograph of fluorescence sensing of different concentration of Hg²⁺+Cu²⁺ mixture ($0 \mu M$, 1 μM , 10 μM , 30 μM and 50 μM) with filter paper based microfluidic device (10 μL of NCDs is drop casted on area **a** which flow to area **b** and **c** (capillary flow through the hydrphophic channels created by wax). Followed by addition of ($5 \mu L + 5 \mu L$) different concentration of Hg²⁺+Cu²⁺ mixture (total concentration, 0 μM , 1 μM , 10 μM , 30 μM and 50 μM). Area **b** and **c** is loaded with vitamin C(VitC) and trisodium citrate(SC) respectively. The photogarph are captured under 365 nm UV lamp.

Fluorescence materials	Analyte	Detection limit	Linear range	Reference
DNA-AuNP	Hg ²⁺	25nM	0.05-2.5µM	S1
CN-DPA	Cu ²⁺	20μΜ	0- 5 μΜ	S2
CDs	Cu ²⁺		10 -90 μM	S3
CDs	Cu ²⁺	20nM	0.0 -30 μM	S4
N-CDs	Hg ²⁺	0.23 μM	0-25µM	S5
NCDs	Hg ²⁺	0.65 μM	0.001-5µM	S6
NCDs	Hg ²⁺	6.2 nM	0.001(1 nM)- 8µM	This Work
NCDs	Cu ²⁺	2.304nM	0.001(1 nM)-22 μM	This Work

Table S1. Fluorescence Hg²⁺ or Cu²⁺ sensing efficiency comparison for different materials

References

- 1 C.Liu, W.HuangandH. T. Chang, *Langmuir*, 2008, 24, 8346-8350.
- 2 Y.Li, X. Zhang, B. Zhu, Xue, Zhu, J and Z. W. Tan, *Analyst*, 2011, **136**, 1124-1128.
- 3 S.Zhang, Q.Wang, G.Tian and H. Ge, *Materials Letters*, 2014, 115, 233-236.
- Q.Liu, N. Zhang, H.Shi, W. Ji, X.Guo, W. Yuan and Q. Hu, New J. Chem., 2018, 42, 3097-3101.
- 5 R. Zhang and W. Chen, *Biosensors and Bioelectronics*, 2014, **55**, 83-90.
- 6 G.Ren, Y.Meng, Q.Zhang, M.Tang, B.Zhu, F.Chai, C. Wang and Z. Su, New J. Chem., 2018, 42, 6824-6830.